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Elemental composition of PM_{2.5} in Shiprock, New Mexico, a rural community located near coal–burning power plants and abandoned uranium mine tailings sites

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ABSTRACT

Fine particulate matter (PM_{2.5}) was collected in Shiprock, New Mexico, a small community located near two coal-fired power plants and numerous abandoned uranium mine tailing sites. Eleven PM_{2.5} samples were collected for 96 h over three sampling periods (April/May 2009, November 2009, and October/November, 2010). Nine samples were analyzed for 64 elements using inductively coupled plasma–mass spectrometry. B, Bi, Cu, Pb, Sb, Sn, and Zn were observed in at least eight samples at levels indicative of anthropogenic enrichment (enrichment factors between 30 and 650). All the seven elements could be explained by coal–combustion processes. B, Bi, and Sb are enriched in coals; Cu, Pb, Sn, and Zn are chalcophile–lithophile or chalcophile elements, all with appreciable affinity for sulfur, a component of coal. Principal component analysis also supported these findings. Four major sources (percent variance) were identified: soil (61%), coal combustion (17%), industrial (11%), and sea salt (5%). Concentrations of elements associated with coal combustion in Shiprock were lower than levels observed in other industrially influenced cities. This was explained by Shiprock's location west of the power plants. Back trajectories indicated that winds arrive to Shiprock from the W, SW, and NW, but the power plants are located to the east (upwind) of the city. Samples were also analyzed for uranium (0.002–0.02 ng/m³) and other metals associated with mine tailings (Sr, Mo). All metals were detected but at low levels, and concentrations did not vary predictably with wind direction. Hence, the tailings sites could not be attributed as the source.

Keywords: Elemental analysis, enrichment factors, ICP–MS, PM_{2.5}, principal component analysis

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1. Introduction

Atmospheric particulate matter (PM) has long been associated with adverse health effects, especially respirable particulate matter or PM_{2.5}, particles ≤2.5 μm in aerodynamic diameter. When inhaled, these tiny particles are small enough to reach the lung's alveoli (Dockery, 2009) and have been linked to respiratory problems, cancer, and premature death (Dockery et al., 1993; Zmirou et al., 1998). In addition to size, particle composition can also contribute to PM_{2.5} toxicity. For example, polycyclic aromatic hydrocarbons in diesel exhaust are probable human carcinogens (Stayner et al., 1998; Mills et al., 2005) and trace metals, when bound to particles, have been associated with lung and cardiopulmonary disease (Cancio et al., 2008; Leili et al., 2008).

The trace metal composition of PM_{2.5} is of particular concern in areas near mining operations or industrial facilities because toxic metals from these sources can contaminate the region's atmospheric dust and particulate matter (Samara et al., 2003; Quiterio et al., 2004; Querol et al., 2007; Csavina et al., 2012). Such impacts have been well documented in large urban centers such as Beijing, China (He et al., 2001; Yuan et al., 2008); Ulsan, Korea (Lee and Hieu, 2011); Agra, India (Kulshrestha et al., 2009); and New York City, United States (Qureshi et al., 2006). Fewer studies have monitored PM_{2.5} trace metal concentrations in small cities, rural communities, or remote areas (e.g., see Gao et al., 2002; Singh et

al., 2002; Liu et al., 2005; Kulshrestha et al., 2009; Na and Crocker, 2009), in part, because such areas often lack industrial influences. However, analysis of PM_{2.5} elemental composition in small communities is warranted when they are affected by local pollution sources.

In this work, the concentration and elemental composition of PM_{2.5} were examined in Shiprock, New Mexico, a small community (8 800 people) located on the Navajo Reservation in the Four Corners region of the U.S. Southwest. Shiprock was chosen as a study site because of its close proximity to two coal-fired generating stations (Figure 1): the Four Corners Power Plant (FCPP, completed in 1970) and the San Juan Generating Station (SJGS, completed in 1982). At the time of this study (2009–2010), FCPP operated five units and SJGS operated four units with annual generating capacities of 1 478 and 1 646 MW, respectively (PNM, 2014). In 2013, to facilitate compliance with the Clean Air Act and the U.S. Environmental Protection Agency (EPA), three of five units at FCPP were decommissioned, and the Public Service Company of New Mexico filed a notice to abandon two units at SJGS by 2017 (PNM, 2014). Shiprock is also located near a high-density region of abandoned uranium mine (AUM) tailings sites (Figure 1). The AUM tailings sites are left over from two “boom and bust” uranium mining cycles in the early 1940s and late 1970s. Both surface (open pit) and underground mining processes were used, producing an overburden of soil and rock wastes. The sites have yet to be

remediated, posing contamination risks to soil, water, and air. The goal of this work was to study the air–quality impacts of these anthropogenic sources by analyzing PM_{2.5} samples collected in Shiprock for enrichment of elements associated with coal–fired power plant emissions and AUM tailings sites.

2. Materials and Methods

2.1. Sample collection

PM_{2.5} samples were collected at the Navajo Nation EPA air monitoring station on the Dine College Campus in Shiprock, NM (Figure 1). Instrumentation included a meteorological station for hourly measurements of wind speed and direction and a filter–based chemical speciation monitor (SuperSASS, Met One Instruments, Grants Pass, OR) for collection of PM_{2.5}. The monitor and meteorological station were housed together on the roof of a small building ~3.5 m above the ground. The PM_{2.5} monitor contains eight sampling inlets, two of which were operated simultaneously, each with a dedicated flow–controlled pump (6.7±0.5 Lpm). A sharp–cut cyclone impactor was used to remove particles >2.5 µm in diameter. PM_{2.5} samples were collected on pre–weighed Teflon filters (47 mm), which were preloaded into canisters in an air–filtered hood, then transported to the sampling site in coolers.

Nine PM_{2.5} samples (Table 1) were collected in three month–long sampling periods in spring 2009, fall 2009, and fall 2010. These months were selected because they are typically the driest and windiest months of the year, increasing the probability of high PM_{2.5} levels. June through August comprise the wet (monsoon) season in this region. To ensure sufficient mass, collection times were typically 96 h (~38.7 m³ of air). Two filters, housed in adjacent canisters, were co–exposed during each 96–h period. At the end of each sampling period, canisters were returned to the laboratory in coolers (~4 °C). Filters were removed from the canisters in an air–filtered hood and stored in a freezer until analyzed. Four field blanks were collected during each sampling period. Field blank filters were loaded into canisters and

transported into the field in the same coolers as the samples and remained in the coolers (in the field) during the month–long sampling period.

2.2. Gravimetric analysis

Gravimetric analysis of the PM_{2.5} filters was conducted at Chester LabNet (Tigard, OR) or Arizona State University (Tempe, AZ). Filters were weighed using a microbalance (±0.0001 mg) under humidity and temperature controlled conditions. PM_{2.5} concentrations were calculated by dividing the mass (µg) by the volume of air sampled (m³) during the 96–h collection period. Particulate mass was not corrected for field blank exposures (≤5% of the sample mass).

2.3. Elemental analysis

Elemental concentrations of 64 trace elements were determined using a double–focusing magnetic sector inductively coupled plasma–mass spectrometer (ICP–MS, ThermoFinnigan ELEMENT2, Bremen, Germany). Details of the instrumental settings, analytical parameters, and filter digestion protocols are described elsewhere (Upadhyay et al. 2009; Upadhyay et al., 2011). In brief, 70% HNO₃ (4.0 mL), 38% HCl (0.9 mL), and 48% HF (0.1 mL) were used in conjunction with an optimized microwave temperature protocol. The digest was diluted to a final volume of 25 mL and partitioned into aliquots for analysis by high resolution ICP–MS. Each element was measured three times yielding an average concentration, standard deviation, and relative standard deviation (%RSD). Co–exposed filters were averaged to yield a single concentration per sample. If this value was below the detection limit (DL), it is reported as <(0.5×DL) in the text and replaced with 0.5×DL in the calculations. All reported concentrations were blank–corrected. Two National Institute of Standards and Technology (NIST) standard reference materials (SRMs)—San Joaquin Soil (SRM 2709) and Urban Dust (1649a)—were used as quality control checks for digestion and analysis.

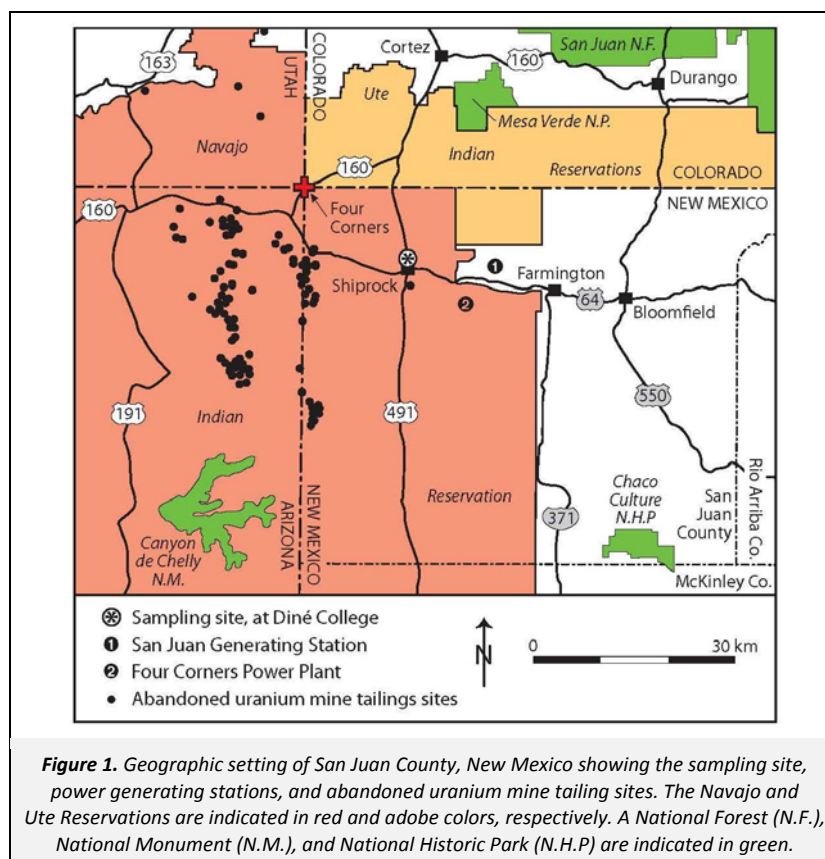


Figure 1. Geographic setting of San Juan County, New Mexico showing the sampling site, power generating stations, and abandoned uranium mine tailings sites. The Navajo and Ute Reservations are indicated in red and adobe colors, respectively. A National Forest (N.F.), National Monument (N.M.), and National Historic Park (N.H.P) are indicated in green.

Table 1. PM_{2.5} sampling information. Two co-exposed filters were averaged for each sample. The three samples in Shiprock 1 were pooled into a single sample before analysis. All other samples were analyzed individually

Period	Sample	Dates (Sunday–Wednesday)	Collection Time (h)
Shiprock 1	1a	April 12–15, 2009	96
	1b	April 19–22, 2009	83
		April 26–29, 2009	(failure)
	1c	May 3–6, 2009	96
Shiprock 2	2	November 1–4, 2009	96
	3	November 8–11, 2009	96
	4	November 15–18, 2009	96
	5	November 22–25, 2009	96
	6	October 17–20, 2010	96
Shiprock 3	7	October 24–27, 2010	96
	8	October 31–November 3, 2010	96
	9	November 7–10, 2010	96

2.4. Principal component analysis

Principal component analysis (PCA) was used as a statistical tool to identify the sources of ambient particulate matter (Hopke, 1991; Upadhyay et al., 2011). In this approach, a large dataset is reduced to a smaller number of independent components. The variables that are closely related via the factor loadings (or correlation coefficients) are interpreted as the principal components (PCs). Usually, a Varimax rotation of the factor loadings is performed to maximize the correlation coefficients near zero or one while keeping the variance and the communality explained by the components unaffected (Henry et al., 1984). The PCs containing tracer chemical components with high correlation coefficients can then be interpreted as sources of pollutants. Varimax rotated PCA was performed using a statistical package SPSS (version 20). PCs with eigenvalues >1 were retained.

2.5. Wind and meteorological analyses

Wind direction and velocity were analyzed using windrose diagrams (Lakes Environmental WRPLOT View, Version 7.0.0). Back trajectories for air parcels arriving in Shiprock during the 96-h collection period were computed using NOAA HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (Draxler and Rolph, 2012; Rolph, 2012). Simulations were computed at 500 m above ground level using the EDAS dataset.

3. Results and Discussion

3.1. PM_{2.5} concentrations

The average PM_{2.5} concentration was 7.0 µg/m³ (range=3.8–11.6 µg/m³) during the three sampling periods (see the Supporting Material, SM, Table S1). No precipitation was recorded during sample collection. PM_{2.5} concentrations were below the yearly national average reported by Bell et al. (2007) for 187 U.S. counties between 2000 and 2005 (14.0±0.2 µg/m³) and significantly below the U.S. EPA (2013) 24-h standard (35 µg/m³). The Navajo EPA operated a PM₁₀ monitoring station at the same site as our study. Twenty-four hour PM₁₀ levels during our sampling periods ranged from 11.6 to 36.6 µg/m³ (average=25 µg/m³); annual PM₁₀ concentrations were 24.5 and 19.5 µg/m³ in 2009 and 2010, respectively (personal communication, Navajo EPA, 2012).

3.2. Elemental concentrations

PM_{2.5} samples were analyzed for 64 trace elements using ICP–MS; 21 were below detection limits in all nine samples (Au, Dy, Er, Eu, Gd, Hf, Ho, In, Ir, Nb, Os, Pd, Pt, Re, Rh, Sm, Ta, Tb, Tm, W, Yb)

and are not discussed further. Concentrations of the remaining 43 elements, in each of the nine samples, are reported in Table S2 (see the SM). In Table 2, we report the concentrations of the most frequently observed elements, those detected in eight or nine PM_{2.5} samples. These 25 elements accounted for 92.5 to 99.9% of the total mass of the 43 detected elements (average=98.7%). The highest concentrations were observed for aluminum, iron, calcium, potassium, and magnesium followed by sodium and titanium.

In Table 3, we report concentrations of 18 metals associated with coal-fired power plant emissions and/or uranium tailings waste. The 14 metals associated with power plant emissions were those reported in toxic release inventories (on-site, fugitive and point source air emissions) for the Four Corners Power Plant and San Juan Generating Station in 2009 and 2010 (U.S. EPA, 2012). The 11 metals associated with uranium mine tailings waste were identified in uranium mill tailings in Durango, Colorado (Morrison and Cahn, 1991), which, like Shiprock, is located in the Four Corners region of the U.S. Southwest. With the exception of mercury, which we did not measure due to its volatility and preference for the gas phase, all metals were detected in at least one PM_{2.5} sample, and many were detected in six or more samples. In most instances, variability across samples was small; however, concentration spikes (max/mean>8) were observed for Cr, Mo, and Ni in sample 8.

3.3. Anthropogenic enrichment

To better assess if anthropogenic sources were contributing to the elements detected in the PM_{2.5} samples, enrichment factors were calculated, using aluminum as the reference element (Buat-Menard and Chesselet, 1979; Han et al., 2006; Kuo et al., 2009). For each element X, the enrichment factor (EF) is:

$$EF(X) = \frac{([X]_s/[Al]_s)}{([X]_c/[Al]_c)} \quad (1)$$

where, s indicates sample and c indicates Earth's upper continental crust. Brackets denote concentration (ng/m³ for samples, µg/g for upper continental crust) (Rudnick and Gao, 2005, see the SM, Table S3). In Figure 2, we plot EF values (geometric mean and range over nine samples) for the elements that were detected in at least eight samples (Table 2). The elements are arranged in periodic-table order (left to right), by group then period. For most elements, inter-sample variation was one order of magnitude or less, but for four trace elements (Rb, Sn, Sb, and Bi) variation was 1.5 to 2 orders of magnitude. Individual EF values ranged from 0.1 (Rb) to 1 700 (Sb).

Table 2. Geometric mean, minimum, and maximum concentrations (ng/m³) for elements observed in at least eight of the nine PM_{2.5} samples collected in Shiprock, NM

Sample 1		Samples 2–5			Samples 6–9		
Species		Mean	Min	Max	Mean	Min	Max
Al	89.2	59.2	39.3	113	29.6	16.0	61.4
B	1.54	3.01	1.75	3.91	2.13	1.51	2.68
Ba	1.24	2.71	2.03	3.45	0.88	0.44	1.38
Bi	<0.001	0.04	0.03	0.07	0.01	0.01	0.02
Ca	90.9	49.3	30.3	139	20.8	5.98	48.2
Ce	0.11	0.08	0.05	0.14	0.03	0.01	0.07
Cu	0.27	0.72	0.50	1.02	0.28	0.13	0.46
Fe	70.8	31.5	20.4	63.6	31.8	5.57	105
K	42.2	48.2	38.6	73.9	16.5	5.29	39.2
La	0.05	0.04	0.03	0.07	0.01	0.004	0.03
Mg	21.6	11.5	8.39	20.7	4.99	2.10	9.87
Mn	1.44	0.81	0.57	1.60	0.56	0.17	1.00
Na	9.72	15.7	9.36	33.9	9.98	7.26	16.6
Nd	0.04	0.03	0.02	0.06	0.01	0.002	0.03
P	1.26	1.74	1.66	2.32	0.94	0.22	2.66
Pb	0.48	0.65	0.39	1.04	0.29	0.20	0.47
Rb	0.13	0.16	0.09	0.29	0.01	<0.001	0.06
Sb	0.03	0.24	0.14	0.36	0.12	0.06	0.18
Sn	0.02	0.16	0.13	0.21	0.15	0.10	0.37
Sr	0.55	0.41	0.31	0.67	0.15	0.03	0.37
Th	0.01	0.01	0.01	0.03	0.004	<0.001	0.01
Ti	6.06	3.33	2.16	5.87	0.95	0.18	2.37
V	0.30	0.28	0.21	0.50	0.13	0.06	0.20
Y	0.03	0.02	0.02	0.04	0.01	0.004	0.02
Zn	0.92	2.27	1.22	5.67	0.47	0.32	0.78

Table 3. Geometric mean, minimum, and maximum concentrations (ng/m³) in PM_{2.5} samples (nine total) for metals associated with air emissions from coal-fired power plants (PP^a) and/or uranium mine tailings waste (UM^b)

Species	Source(s)	No. of Samples	Mean	Min	Max
Ba	PP/UM	9	1.51	0.44	3.45
Cu	PP/UM	9	0.42	0.13	1.02
Fe	UM	9	34.6	5.57	105
Mn	PP/UM	9	0.74	0.17	1.6
Pb	PP/UM	9	0.44	0.20	1.04
Sb	PP	9	0.14	0.03	0.36
Sr	UM	9	0.27	0.03	0.67
V	PP/UM	9	0.20	0.03	0.50
Zn	PP	9	1.02	0.32	5.67
Co	PP	6	0.02	0.01	0.05
Cr	PP	6	0.27	0.08	12.5
Ni	PP	6	0.24	0.05	1.96
As	PP/UM	5	0.18	0.09	0.27
Se	PP/UM	4	0.51	0.17	2.11
U	UM	4	0.01	0.002	0.02
Mo	UM	2	0.05	0.003	0.46
Be	PP	1	0.01	0.01	0.01
Hg ^c	PP				

^a PP metals were listed in the toxic release inventories (on-site, fugitive and point source air emissions) for the Four Corners Power Plant and San Juan Generating Station in 2009 and 2010 (U.S. EPA, 2012)

^b UM metals were approximated from uranium mill tailing samples analyzed in Durango, CO (Morrison and Cahn, 1991)

^c Hg was not measured in PM_{2.5} samples due to its volatility and preference for the gas phase

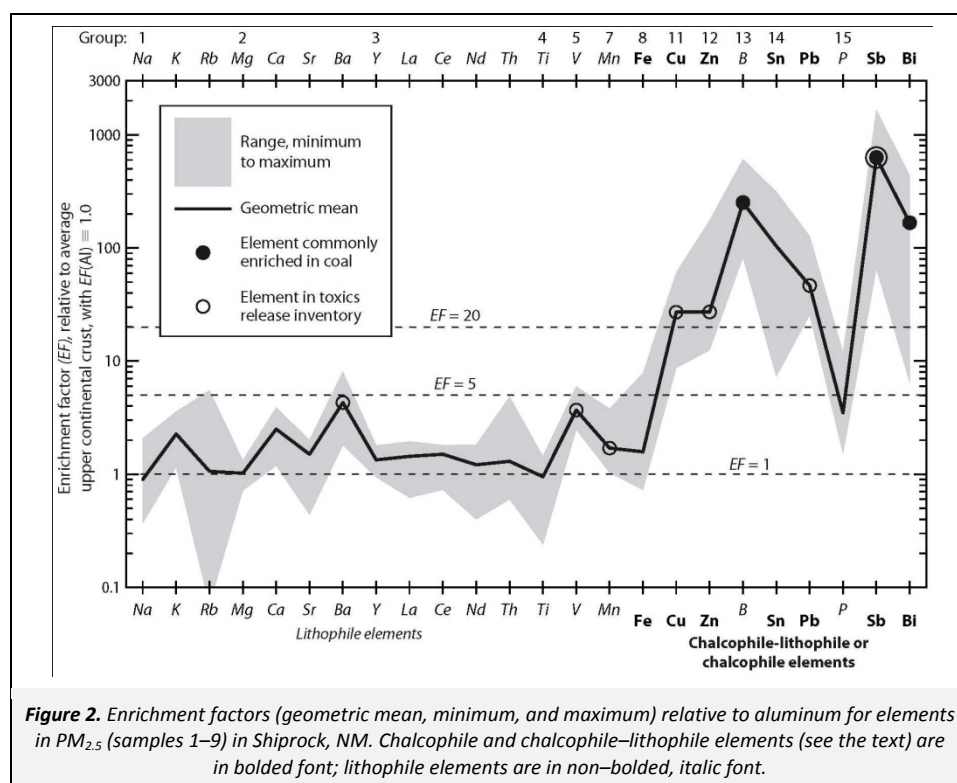


Figure 2. Enrichment factors (geometric mean, minimum, and maximum) relative to aluminum for elements in PM_{2.5} (samples 1–9) in Shiprock, NM. Chalcophile and chalcophile–lithophile elements (see the text) are in bolded font; lithophile elements are in non–bolded, italic font.

Geochemists commonly use a semiquantitative classification in which chalcophile elements, those with appreciable affinity for sulfur, are distinguished from lithophile elements, those whose principal affinity is for silicate and oxide phases (White, 2013). These categories overlap; some elements (notably Fe) have both chalcophile and lithophile tendencies. Of the 24 elements plotted in Figure 2, seventeen—Na through Mn, B, and P—are exclusively lithophile. The other seven—Fe, Cu, Zn, Sn, Pb, Sb, and Bi—are chalcophile or mixed chalcophile–lithophile. All but one (B) of the 17 lithophile elements had EF values < 5, indicative of natural sources with proportions approximating those found in the upper continental crust. Moreover, the flat part of the curve from Y through Ti (Y, La, Ce, Nd, Th, Ti) suggests that in the PM_{2.5} samples these elements reside in minerals such as apatite, Fe–Ti oxides, zircon, and monazite, all relatively resistant to weathering and not strongly fractionated by sedimentary processes.

EF values > 5 are generally indicative of enrichment due to anthropogenic sources (Wu et al., 2007). Seven elements were in this group (EF > 20). Three (B, Sb, and Bi) were strongly enriched with EF values between 100 and 650; these elements have been shown to be enriched in coals (Goodarzi and Swaine, 1993; Cox, 1995; Xu et al., 2004; Orem and Finkelman, 2005) and in fly ash generated during coal combustion at power stations (Querol et al., 1995). Four metals (Cu, Zn, Sn, and Pb) had EF values between 20 and 100; these four (as well as Sb and Bi) are chalcophile–lithophile or chalcophile elements, all with affinity for sulfur. Sulfur is contained in subbituminous coals, which is the principal coal type used at FCPP and SJGS; hence, coal–fired power plant emissions are a plausible source for all seven enriched elements. Correspondingly, the four heavy metals in this group (Cu, Zn, Pb, and Sb) were reported in the 2009 and 2010 toxic release inventories for these power plants (Table 3, U.S. EPA, 2012). Residential coal burning, a common source of heat on the Navajo Reservation (Bunnell et al., 2010), may also be a contributing source.

3.4. PCA analysis

Elemental data (25 elements) were also analyzed by PCA (Figure 3, see the SM, Table S4). The first principal component accounting for 61% of the variance is interpreted as soil based on

the strong contributions of soil elements like Al, Sr, Ca, Ce, La, and Ti. This is consistent with the low enrichment factor of these elements indicating an upper crustal source as well as the attribution in other studies in the Southwest (e.g. Majestic et al., 2009; Upadhyay et al., 2011). It is surprising that this factor is so dominant (>50% of variance) in PM_{2.5}, as this was not the case in earlier studies of the Southwest (Majestic et al., 2009).

The next two components are interpreted as anthropogenic sources. PC2, which accounts for 17% of the variance, is dominated by Sb, Sn, Bi with some contribution by B. These elements, as discussed earlier, are enriched in coals (Goodarzi and Swaine, 1993; Cox, 1995; Xu et al., 2004; Orem and Finkelman, 2005) and in fly ash from coal–fired power plants (Querol et al., 1995); therefore, we attribute this factor to coal combustion. PC3, which accounts for 11% of the variance, has smaller contributions. Given the contributions of Zn and Pb, anthropogenic sources are likely; in a Phoenix study, Ramadan et al. (2000) attributed Zn and Pb (along with Cu and As) to non–ferrous smelting processes. The fourth factor, accounting for a mere 5%, is mainly sodium and could be sea salt, also observed in Phoenix (Ramadan et al., 2000). Together, PC3 and PC4 suggest that Shiprock's PM_{2.5} composition may be influenced by regional sources, specifically Phoenix, AZ. Additional evidence for regional influences is presented in the next section.

3.5. Wind analyses

Air parcel back trajectories (96–h) were calculated for samples 2–9 using the NOAA HYSPLIT model (Draxler and Rolph, 2012; Rolph, 2012). (Because sample 1 pooled together three samples over a month–long sampling period, trajectories were not computed.) As shown in Figure S1 (see the SM), air parcels generally arrived from the NW and SW. Windrose diagrams, which plot local wind velocities and directions, provided similar results (Figure S2). During the three sampling periods, maximum wind velocities were between 9.2 and 12.3 m/s; minimum wind velocities were between 3.4 and 8.1 m/s, and winds were predominantly from the NW, SW, or SE. Collectively, these wind patterns suggest that during sampling, Shiprock was generally upwind of the coal–fired power plants (located east of Shiprock).

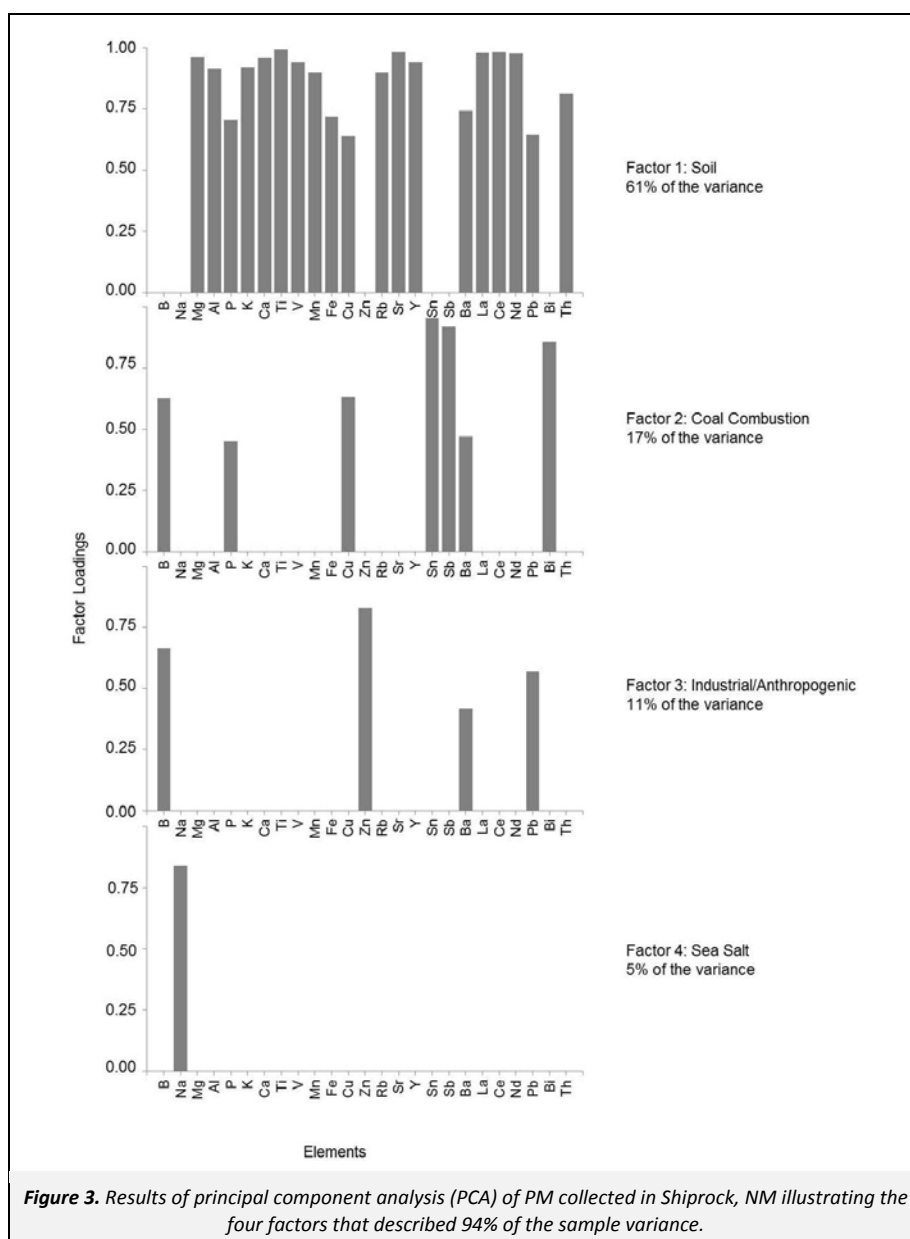
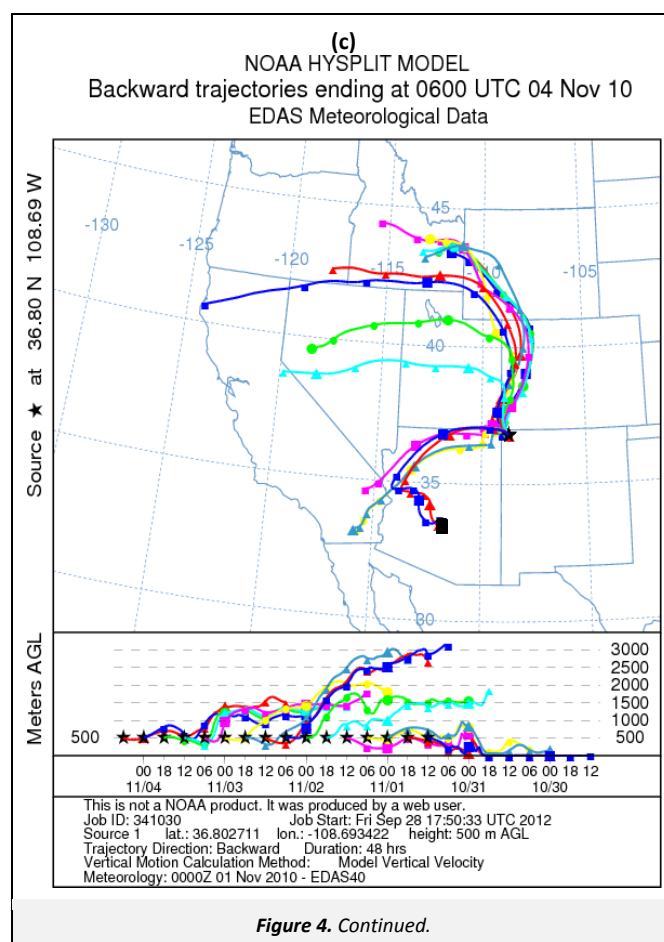
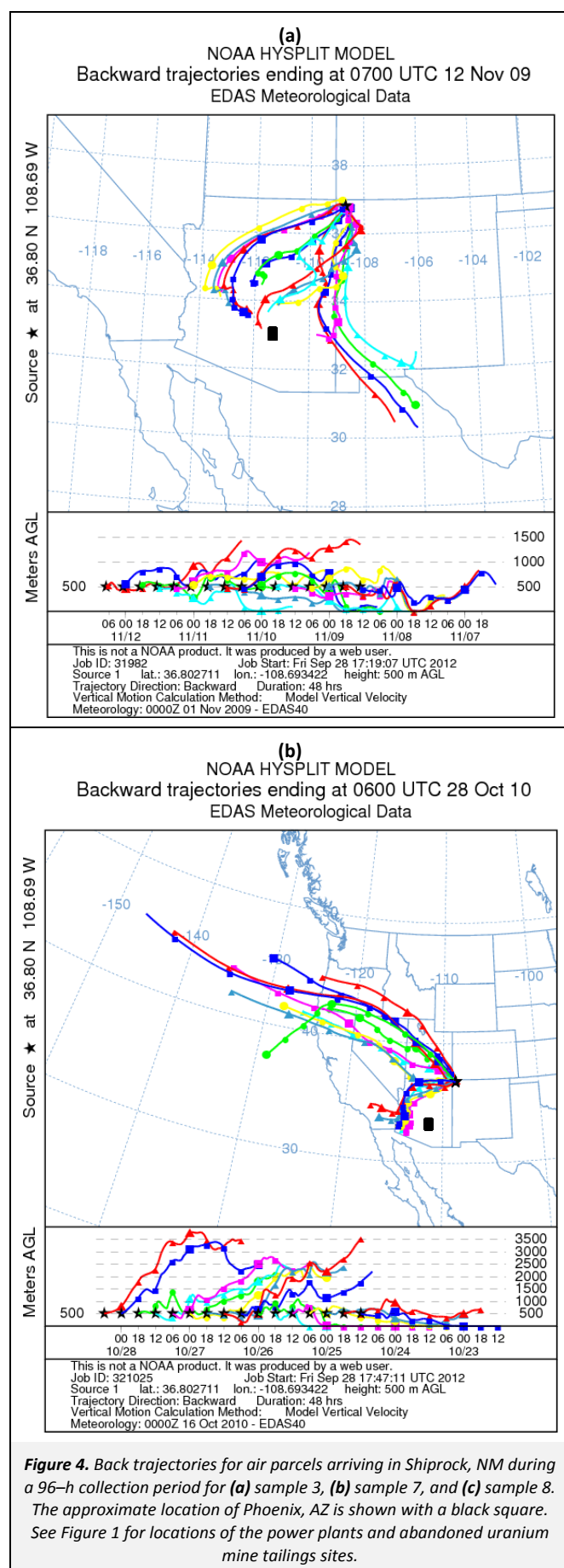


Figure 3. Results of principal component analysis (PCA) of PM collected in Shiprock, NM illustrating the four factors that described 94% of the sample variance.

HYSPLIT trajectories also suggest that regional sources may be contributing to PM_{2.5} in Shiprock. In Figures 4A and 4B, we show HYSPLIT trajectories for samples 3 and 7, the samples that had the highest and lowest total concentrations of the 25 elements listed in Table 2 (Σ_{25} elements=466 and 49 ng/m³, respectively). In sample 3, 22 of the 25 elements reported in Table 2 were detected at their highest or second highest levels (all but Fe, P, and Zn); in sample 7, 21 of the 25 elements were detected at their lowest or second lowest levels (all but B, Bi, Na, and Zn). The highest levels were observed when trajectories involved Phoenix, Arizona, a large metropolitan area (Figure 4A) known for high PM_{2.5} episodes attributed to combustion sources (motor vehicles, vegetative burning, and diesel exhaust) and, to a lesser extent, coal-fired power plants and non-ferrous smelters (Ramadan et al., 2000; Upadhyay et al., 2011). Conversely, the lowest levels were observed when trajectories originated over the Pacific Ocean, the Pacific Northwest, or western Arizona (Figure 4B). The intermediate levels detected in the other samples were largely combinations of the trajectories shown in Figures 4A and 4B (see the SM, Figure S1). In Figure 4C, we also show back trajectories for sample 8, in which concentrations spiked for Cr, Mo, and Ni. These trajectories also suggest regional influences by Phoenix and/or eastern Colorado. In South Phoenix, Upadhyay et al. (2011)

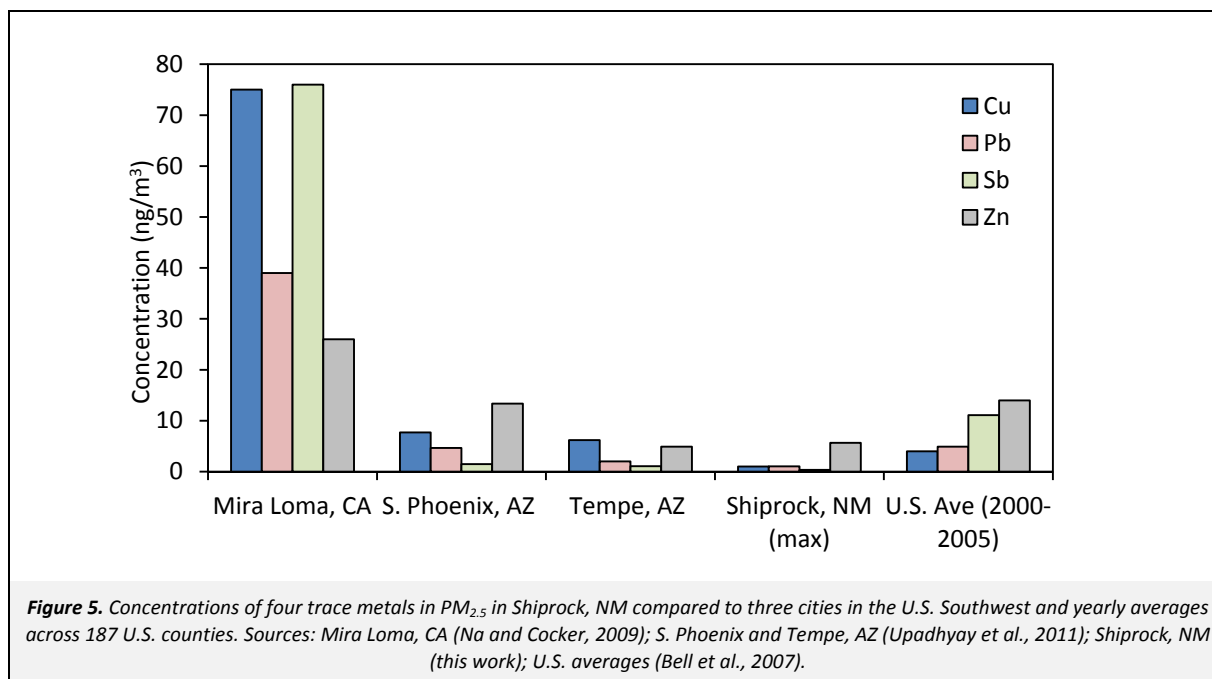
reported anthropogenic enrichment of Cr and Ni in PM_{2.5} samples as well as As, Ba, Cu, K, Pb, Sb, Se, Sr, and Zn, consistent with regional influences by Phoenix.

In contrast to the power plants, Shiprock is located downwind (east) of the uranium mine tailings sites (Figure 1). The two highest uranium concentrations in this study (both 0.02 ng/m³) were observed in samples 2 and 4 (see the SM, Table S2); in each case, HYSPLIT back trajectories (Figure S1) show that these air parcels passed over tailings sites. However, samples 3 and 6–9 all had low levels of uranium (<0.0002 ng/m³), and these also passed over tailings sites; hence, the wind data are inconsistent. Similarly, the windrose plots for Shiprock 2 (containing samples 2 and 4) show local winds coming largely from the SE (see the SM, Figure S2), not the expected direction if windblown tailings are the uranium source. Although these data cannot rule out the tailings sites as the uranium source, they do not clearly support this conclusion. Similar inconsistencies exist for Fe, Sr, and Mo, which are also associated with uranium mine tailings (Table 3). These metals had the highest concentrations in samples 8 (Fe, Mo) or 3 (Sr), where winds passed over the tailings sites, but all had their lowest levels in sample 7, even though this trajectory also passed over some sites.



3.6. Comparisons with other cities

To place these results in perspective, we compare maximum concentrations for four enriched metals in Shiprock PM_{2.5} (Cu, Pb, Sn, and Zn) to mean values measured in three cities in the U.S. Southwest and to average annual values reported for 187 U.S. counties between 2000 and 2005 (Bell et al., 2007) (Figure 5). The highest contaminant levels were observed in Mira Loma, a semi-urban city between Los Angeles and the San Bernardino Mountains, heavily influenced by Los Angeles pollution (Na and Cocker, 2009). Contaminant levels were lower in South Phoenix, an area known for high PM levels, and Tempe, a southeastern suburb of Phoenix (Upadhyay et al., 2011). Shiprock values were lower than all of these cities for copper, lead, and tin, and roughly equal to Tempe for zinc. Similarly, elemental concentrations of copper, lead, and zinc in Shiprock PM_{2.5} were the same or less than values reported for three small eastern U.S. cities (populations <7 000): Yorkville, Georgia (Liu et al., 2005); Sandy Hook, New Jersey (Gao et al., 2002), and Centreville, Alabama (Liu et al., 2005). Thus, although industrial contamination is evident in Shiprock PM_{2.5}, contaminant levels are generally low when compared to other smaller cities and U.S. national averages. These results are also low when compared to large urban areas. For example, in Beijing, China concentrations of 35, 304, and 480 ng/m³ were reported for copper, lead, and zinc, respectively (He et al., 2001); in Agra, India concentrations for these three metals were 200, 1 100, and 900 ng/m³, respectively (Kulshrestha et al., 2009). Both Shiprock's topography (lack of mountains to trap in pollutants) and location (upwind of the coal-fired power plants) may explain these relatively low pollution levels. To our knowledge, there were no variations in power plant emissions during sampling, which could also explain low pollution levels, but we could not confirm this with emissions data.



Uranium concentrations were also low. Although detected in four of nine PM_{2.5} samples (0.002 to 0.02 ng/m³), uranium concentrations were lower than or similar to levels reported in other cities not near tailings sites. For example, in Nogales, Arizona, uranium in PM_{2.5} samples ranged between 0.09 and 0.25 ng/m³ (unpublished), whereas on the Arizona State University campus in Tempe, Arizona, concentrations up to 0.2 ng/m³ were reported (Upadhyay et al., 2009). In Lodz, Poland, uranium concentrations of 0.31 ng/m³ have been reported (Bem et al., 2003).

4. Conclusion

The elemental composition of PM_{2.5} in Shiprock, NM was analyzed for evidence of anthropogenic influence. Shiprock was chosen as a study site because of its close proximity to two coal-fired power plants (east of Shiprock) and numerous abandoned uranium tailings sites (west and southwest of Shiprock). Seven elements were anthropogenically enriched in at least eight of nine samples (B, Bi, Cu, Pb, Sb, Sn, and Zn), and occasionally high concentrations were observed for five heavy metals (Zr, Cr, Ni, Se, and Mo). Local coal-burning processes offer a plausible source for these contaminants; however, regional contributions from industrial and other anthropogenic activities are also likely. Contaminant levels were low compared to other cities, most likely a result of Shiprock's topography and location upwind of the power plants. Low levels of uranium were detected in four of nine samples; however, the wind patterns were not consistent with the abandoned tailings sites being the major source of this uranium.

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Supporting Material Available

Detailed PM_{2.5} sampling information and concentrations (Table S1), Elemental concentrations for 43 elements (Table S2), Upper crustal abundances used in EF calculations (Table S3), Factor

loadings with four principal components for 25 elements and percent variance (Table S4), HYSPLIT trajectories for nine samples (Figure S1), Windrose diagrams for Shiprock samples 1–3 (Figure S2). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

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